

THE EFFECT OF CO₂ PARTIAL PRESSURE ON GASIFICATION REACTIVITY

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Keywords: Reactivity; CO₂ partial pressure; thermal desorption methods.

INTRODUCTION

The mechanisms by which varying partial pressures of oxidant gases affect char reactivity remains a matter of controversy. In the current communication we explore the effect of CO₂ partial pressure on the resultant populations of intermediate oxygen complexes on char surfaces and their relationship to reactivity.

EXPERIMENTAL

The samples used in the experiments were Wyodak subbituminous coal char samples produced from coal obtained from the Argonne Premium Coal Sample Bank [1], and a resin char produced from phenol-formaldehyde resin synthesized in our laboratory. The latter was used as a prototype of a non-mineral matter-containing char. Char samples were produced in a tube furnace in flowing ultrahigh purity helium at 1000°C for two hours.

Partial pressure variation was achieved using CO₂/helium mixtures. All the oxidation and thermal desorption experiments were carried out in the TPD-MS/TGA apparatus. For gasification, the samples were exposed to the CO₂/helium gas mixtures at one atmosphere at a selected temperature to a certain degree of burn-off. The gasification conditions selected for the current work were 825°C, 20% burn-off for Wyodak coal char, and 900°C, 5% burn-off for resin char. The thermal desorptions were all carried out at a heating rate of 50K/min to 1200°C in flowing ultrahigh purity helium carrier gas.

RESULTS AND DISCUSSION

The overall or global reaction order for the char-CO₂ reaction remains a matter of controversy. The typical Langmuir-Hinshelwood-type steady-state rate expressions, as obtained for the Mentser and Ergun [2] oxygen exchange mechanism for example, suggest that the reaction should be first order at low pressures, changing gradually to zeroth order behavior at higher pressures. Turkdogan and Vinters [3] reported half-order dependence at pressures less than 10 atm, and zeroth order behavior at pressures of 10-20 atm. Koenig *et al.* [4] also reported half-order behavior. Blackwood and Ingeme [5] reported that at high pressure, the gasification rate remains dependent on CO₂ partial pressure to a positive order. On the other hand, the gasification data of Johnson [6] for a bituminous coal char in CO/CO₂ mixtures over the range 2-35 atm, showed a decreasing effect of CO₂ pressure on the gasification rate at high pressures. A similar trend was reported by Golovina [7], who reported first order behavior at near-atmospheric pressure, tending to zeroth order over the 3-10 atm range, followed by decreasing gasification rate with CO₂ partial pressure in the 20-40 atm range. In the current work, the apparent reaction orders observed for CO₂ partial pressures of one atmosphere and less, were 0.71 for resin char and 0.60 for Wyodak coal char.

Obviously, the apparent reaction order varies considerably with the nature of the char and gasification conditions, which makes it difficult to compare data from various sources and predict/correlate reactivity. Moreover, most of the interpretive/correlative models are based on one or two-site models which tend to oversimplify the nature of char surfaces and mechanisms. Most chars exhibit distinctly energetically heterogeneous surfaces which can have a significant effect on the behavior of the apparent reaction order. For example, Calo and Perkins [8] demonstrated that surface heterogeneity can result in half-order behavior under certain conditions, and that the observed reaction order depends in a complex manner on the nature of the surface. For these reasons, here we focus on investigations of correlations between reactivity and populations of the intermediate oxygen surface complexes which desorb to gasify the char.

Figure 1 presents CO TPD spectra for resin char samples gasified in various CO₂/He mixtures. As shown, the broad desorption peak is centered at about 1010°C. The total amount of oxygen surface complexes increases with CO₂ partial pressure, but not homogeneously over the entire TPD spectrum. That is, the higher temperature surface complexes fall off more rapidly than the lower temperature complexes. These observations are consistent with those of Kapteijn *et al.* [9] who reported that increasing the CO₂ partial pressure from 0.1 to 1 atm increased the number of stable, higher temperature complexes more than the low temperature, unstable complexes.

Figure 2 presents the corresponding data for Wyodak coal char samples. The same qualitative behavior observed for resin char is readily apparent, although the desorption is peaked at a lower temperature of about 950°C. In addition, the total amount of oxygen surface complexes is about a factor of three or so greater than for the resin char.

The Rate-Controlling Step. It has been concluded by some workers that CO₂ gasification is

desorption rate-controlled [Marchon *et al.* [10]; Cerfontain *et al.* [11]; Chen and Yang [12]; Calo and Hall [13]; and Mentser and Ergun [2]. However, Kapteijn *et al.* [9] contend that for uncatalyzed CO₂ gasification, two processes are operative: (1) the decomposition of semiquinone/carbonyl surface complexes; and (2) the decomposition of an "out-of plane" oxygen complex which can be formed upon oxidation by CO₂ of a saturated carbon atom adjacent to an edge carbon which is already bonded to an oxygen atom. This latter type of oxygen complex has been shown to cause a substantial weakening of neighboring carbon-carbon bonds, and its decomposition results in the formation of a gas phase CO molecule and a semiquinone-type surface complex. This model explained their step-response data quite well, and supports the earlier mechanistic reasoning of Blackwood and Ingeme [5]. It was also concluded that the relative contribution of the two processes to the gasification rate is controlled by the CO₂ partial pressure.

In order to address the issue of the rate-controlling step in the current work, the following types of experiments were performed. Following gasification, samples were rapidly quenched to room temperature in either pure helium or the reactive gas mixture. This was done to assess whether or not the surface was saturated with oxygen surface complexes at gasification conditions. It was reasoned that if the gasification reaction was not controlled by the desorption step, unoccupied active sites would exist which by cooling in the reactant mixture would form additional oxygen surface complexes as the temperature decreased. Consequently, the resultant TPD spectra would differ from those obtained following rapid quenching in helium.

In Figure 3 are presented the corresponding desorption spectra for resin char following gasification in 1 atm of CO₂. As shown, the two spectra are practically identical. This result implies that gasification in pure CO₂ for resin char under these conditions is indeed desorption rate-controlled. However, as shown in Figure 4, the corresponding spectra following gasification in a 60/40 CO₂/He mixture yielded distinctly different TPD spectra. As shown, the principal difference lies in the low temperature surface complex populations. That is, the CO desorption over the temperature range between 600 and 900°C for the sample cooled down in the reaction mixture is greater than that for the sample cooled in He. This result is interpreted to mean that unoccupied active sites exist during the steady-state gasification in the 60/40 CO₂/He mixture under these conditions. These unoccupied active sites remained unoccupied when the samples were cooled down in He, but were populated with oxygen complexes in cooling down in the reaction mixture. Consequently, it is concluded that gasification departs from desorption rate-control as the CO₂ partial pressure decreases from 1 atm.

Distribution of Desorption Activation Energies. The observation that the population of oxygen surface complexes does not decrease evenly over the entire TPD spectrum suggests that the char surface exhibits a distribution of desorption activation energies. Du *et al.* [14] and Calo and Hall [13] have developed distributed activation energy models for the desorption of oxygen surface complexes from carbons following O₂ and CO₂ gasification. In the current work, the distribution of desorption activation energies was calculated using the method described by Calo and Hall [13]. The relationship between the instantaneous CO desorption rate and the distribution of desorption activation energies can be expressed as:

$$d[\text{CO}]/dt = [\text{C-O}]_0 S(E^*) dE^*/dt \quad [1]$$

where E^* is the local desorption activation energy, as approximated by an instantaneous step at energy E^* , $S(E^*)$ is the desorption activation energy probability density function, $d[\text{CO}]/dt$ is the desorption rate of oxygen surface complexes as CO during TPD, and $[\text{C-O}]_0$ is the total initial (i.e. prior to the initiation of desorption) amount of CO-evolving oxygen surface complexes on the surface. Based on the classical work of Redhead [15], the parameters are related by:

$$E^*/RT = \ln [v_0 T/\beta] - 3.64 \quad [2]$$

which holds for $10^8 < v_0 \beta < 10^{13} \text{ (K}^{-1}\text{)}$, where v_0 is the pre-exponential factor for the desorption rate constant, T is the temperature, and β is the heating rate. Since a TPD experiment gives the instantaneous desorption rate directly, and dE^*/dt can be obtained from Eq. [2], the distribution of desorption activation energies, $[\text{C-O}]_0 S(E)^*$, can be determined from Eq. [1].

The value of the pre-exponential factor, v_0 , was assumed to be a constant. A series of TPD runs was performed at various heating rates from 25K/min to 100K/min for the same oxidized char samples. It was determined that a value of $v_0 = 10^{10} \text{ min}^{-1}$ yielded the best fit in that it produced essentially the same energetic distribution for all the heating rates. This proved to be the best value for both resin and Wyodak char. Consequently, this value was used for the determination of the distributions of desorption activation energies.

Figure 5 presents the resultant desorption activation energy distribution for Wyodak coal char gasified in various CO₂/He mixtures. As can be seen, as the CO₂ partial pressure during gasification decreases, the desorption activation energy distribution of the char also changes.

The same trend was also found for resin char samples gasified in various CO₂/He mixtures. In comparison to the results for Wyodak coal char, the energetic distributions of oxygen surface complexes for the resin char samples are shifted to higher energies. It is also noted that mineral matter (most probably calcium) in the Wyodak coal char plays a significant role in determining the population of the low temperature surface complexes which turn over most rapidly during gasification. The absolute amount of the low temperature oxygen surface complexes is much higher for Wyodak coal char than for the resin char, which contains no mineral matter. Therefore the mineral matter in the Wyodak coal char "catalyzes" the formation of low desorption activation energy surface complexes. This represents the basis of the catalytic effect in this char. This is the principal reason that the reactivity of Wyodak coal char is significantly greater than that for resin char even at lower gasification temperatures.

Correlation of Reactivity. For conditions where the gasification rate is desorption rate-controlled, the reactivity can be correlated using the distribution of desorption activation energies. This is accomplished by integrating the desorption rate over the entire distribution:

$$r = \int_0^{\infty} v_0 \exp(-E^*/RT) [C-O]_0 S(E^*) dE^* \quad [3]$$

Figure 6 presents a parity plot of predicted vs. measured reactivities for Wyodak coal char in one atmosphere of CO₂ as a function of temperature, as determined from Eq. [3] using the desorption activation energy distribution obtained at 825°C. As shown, the agreement is reasonably good. Similar results were obtained for resin char. Therefore, it can be concluded that the correlation of reactivity with the TPD desorption rate is feasible.

SUMMARY AND CONCLUSIONS

The objective of this work was to explore the relationship among reactivity, CO₂ partial pressure, and post-reaction TPD spectra. The results show that CO₂ partial pressure has a significant effect on the population of oxygen surface complexes for both resin and Wyodak coal chars. Generally, the oxygen surface coverage increases with increasing CO₂ partial pressure. It was also determined that gasification reactivity is desorption rate-controlled in 1 atm of CO₂ for both chars. However, as the CO₂ partial pressure decreases, the formation rates of surface complexes become comparable to the desorption rates, and the reaction rate begins to deviate from desorption rate-control.

For heterogeneous char surfaces, the distribution of desorption activation energies can be determined from TPD desorption rates. Prediction/correlation of reactivities from the desorption activation energy distribution is shown to be feasible for the carbon-CO₂ reaction operating under desorption rate-controlled conditions for both resin and Wyodak coal char.

It is possible that the most labile, low temperature oxygen surface complexes that are observed to increase in concentration with increasing CO₂ partial pressure may be of the type hypothesized by Kapteijn *et al.* [9] and Chen *et al.* [16], as being formed by the interaction of CO₂ with existing surface complexes. If this is so, then the thermal desorption methods applied here would reveal a shift or interconversion between labile and stable complexes with increasing pressure. This is a subject of continuing studies.

ACKNOWLEDGEMENT

This work was supported by Grant Nos. DE-FG22-90PC90307 and DE-FG22-91PC91305 from the UCR Program of the U.S. Department of Energy.

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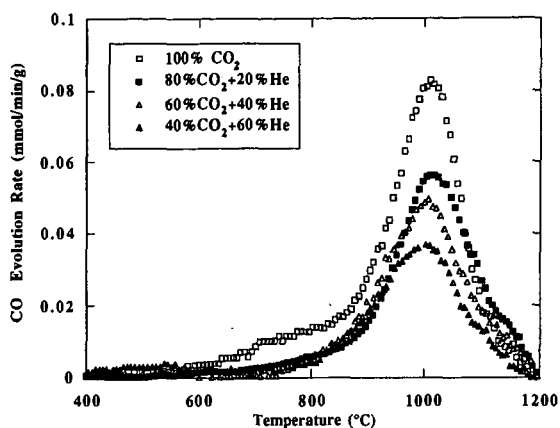


Figure 1. CO TPD spectra from resin char gasified in 1 atm of CO_2/He mixtures at 900°C to 5% burn-off.

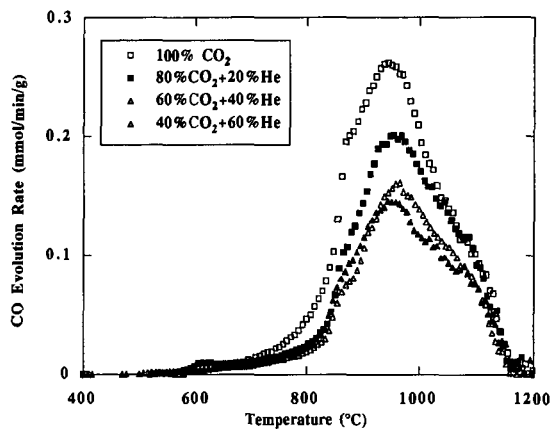


Figure 2. CO TPD spectra from Wyodak coal char gasified in 1 atm of CO_2/He mixtures at 825°C to 20% burn-off.

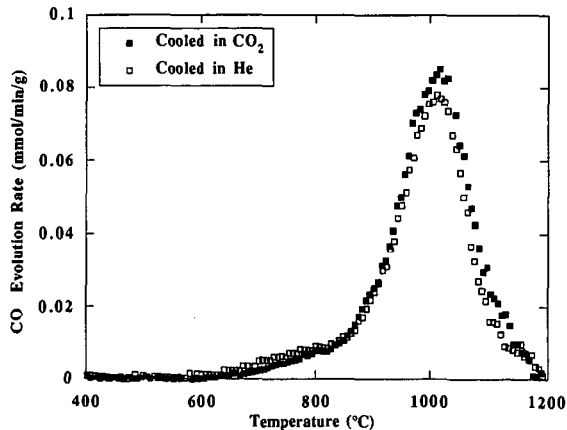


Figure 3. CO TPD spectra from resin char gasified in 1 atm of CO_2 at 900°C to 5% burn-off, following quenching in helium and CO_2 .

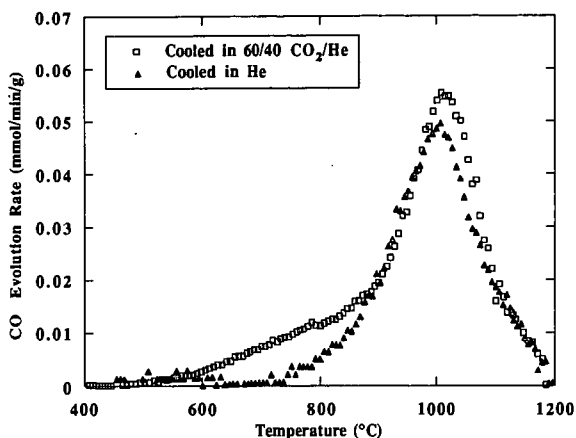


Figure 4. CO TPD spectra from resin char gasified 60/40 CO_2/He at 1 atm, 900°C to 5% burn-off, following quenching in helium and CO_2 .

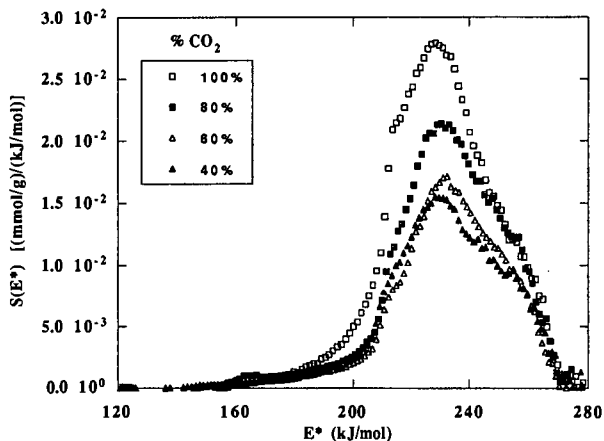


Figure 5. Distributions of desorption activation energies from TPD spectra presented in Figure 2 for Wyodak coal char gasified in CO_2/He mixtures at 825°C, 1 atm to 20% burn-off.

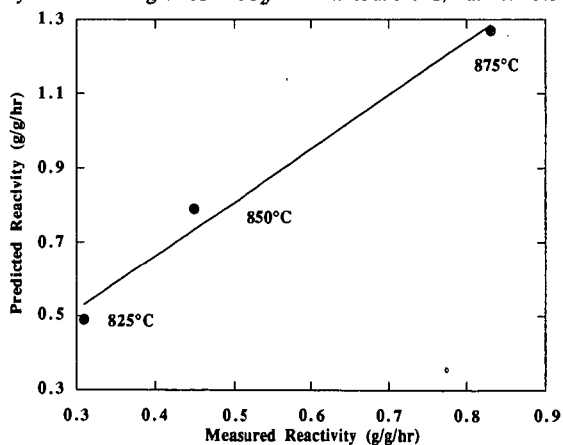


Figure 6. Predicted vs. measured reactivities for Wyodak coal char gasified in 1 atm of CO_2 to 20% burn-off.